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16. ABSTRACT

The capability of an equilibrium speciation model, MINTEQA2, for estimating total dissolved (and, hence, mobile) metals concentrations in the saturated zone below hazardous waste disposal sites was evaluated in laboratory studies. Emphasis was placed on testing the geochemical speciation portion of the model.

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MODELING GEOCHEMICAL PROCESSES ATTENUATING INORGANIC CONTAMINANT TRANSPORT IN THE SUBSURFACE REGION: ADSORPTION ON AMORPHOUS IRON OXIDE

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INTRODUCTION

Many suspected or acknowledged environmental problems are national in scope. In a regulatory context, the ability to resolve these problems is greatly complicated by: (1) current incomplete scientific knowledge concerning the nature and origin of these problems, (2) the wide variety of environments that may be affected by these problems, and (3) the differences that may arise between legal and scientific perceptions of these problems.

As a case in point, recent changes to the Resource Conservation and Recovery Act (RCRA), enacted through the Hazardous and Solid Waste Amendments (November 8, 1984) require the U.S. Environmental Protection Agency (EPA) to develop regulatory programs for the identification and management of hazardous wastes containing metals. In support of the EPA's Office of Solid Waste effort, EPA's Environmental Research Laboratory in Athens, Georgia is developing a computer model to predict transport and transformation of inorganic contaminants in the subsurface environment and evaluate the potential for human exposure in drinking water. From a scientific perspective, the transport of inorganic contaminants is subject to a wide variety of geochemical and hydrological processes, many of which either are poorly understood or require intensive data inputs that are often difficult to obtain even on a site specific basis. As a consequence, one provision for the computer model under development is that the model be applicable in a generic (nationwide) context where the overall uncertainty of model predictions can be quantified.

The requirement for quantifying the uncertainty associated with model predictions leads to a second consideration--the concept of model "validation." In the ideal site-specific situation, the gross uncertainty associated with model predictions can be determined by comparison of model predictions with an established database containing sufficient information to document the variables of interest. Furthermore, error propagation derived from the individual model source terms also would be available. Unfortunately, field testing a coupled transport geochemical speciation model is prohibitively expensive.

The approach with the present effort--the subject of this paper--is to provide a broad spectrum of diverse evidence that, taken together, leads to scientific and regulatory confidence in the model's predictive capability. The present strategy is to include field studies, laboratory investigations and peer review evaluations in sufficient number and detail to offer a convincing argument for the model's predictive accuracy in the face of intense scientific and regulatory scrutiny.

The present investigation was undertaken as one element of a research program to develop and test (validate) methods for predicting the leaching, transport and potential groundwater contamination threat of metals for generically defined land disposal sites. Specifically, the capability of an equilibrium metal speciation model (MINTEQA2) for estimating total dissolved (and hence, mobile) metals concentrations in the saturated zone below hazardous waste disposal sites was evaluated in laboratory studies.

The MINTEQA2 computer code is an updated version of the precursor MINTEQA1 geochemical speciation code (6) that incorporates a diffuse layer electrostatic adsorption model option (12) and a built-in database of intrinsic thermodynamic adsorption constants for a large variety of potential metal contaminants interacting with amorphous iron oxide substrates. The current strategy for testing the geochemical speciation portion of the model is the focus of this paper.

MODELING STRATEGY

The chemical and physical processes governing the partitioning behavior of inorganic contaminants in the subsurface environment may include a large variety of thermodynamic equilibrium, disequilibrium and/or kinetic-limited reactions that are understood from a scientific perspective to only a limited degree. Figure 1 illustrates a schema for incorporating a thermodynamic equilibrium chemical process component into a predictive exposure assessment tool.

Several points should be made before discussing the individual components in figure 1. First, although the model must be generic in nature, the uncertainty associated with individual components necessarily requires assessment on a site-specific basis. Second, the required precision and accuracy for each component is bounded primarily by the least precise, heavily weighted component (that is, if the uncertainty in one major component is $\pm$ 50%, then 4 digit accuracy in a less significant component is unnecessary). Third, where the scientific knowledge is insufficient for quantifying uncertainty, then assumptions used in the effort must be conservative. (Conservative is defined in this paper as protective of the environment). Fourth, a generic approach likely will be composed of both statistically characterized distributions and worst case assumptions.

The uppermost box in figure 1 displays the goal of deriving a defensible partitioning/transport model. The least resource intensive means of achieving this goal depends on resolving and, where necessary, minimizing the uncertainty associated with each of the individual processes at the lowest, practical level of the pyramid in figure 1. For example, resolving the significance of one of the individual chemical processes is best achieved at the laboratory level. If a given process is significant, yet poorly understood, then the probability of making mistakes in field data collection is magnified greatly. The usable results from such a study may be seriously compromised and the wasted resources associated with these mistakes may be orders of magnitude greater than would be encountered in a laboratory setting.

Physico-Chemical Processes Influencing Potential Contaminant Transport

The individual chemical processes in figure 1 represent a compendium of potential known chemical processes that may have a significant impact on the partitioning of inorganic contaminants in the subsurface environment. These processes have been categorized (perhaps artificially) into those that may promote transport and those that may inhibit transport. Of these two categories, those promoting transport are generally the best understood. For example, the thermodynamic relationships among free ion activities, inorganic complexes, and organic complexes have a substantial historical background in the scientific literature. The relationship between free ion activities and complexation with naturally occurring dissolved organic matter (DOM) is much more ambiguous. Although there is substantial on-going research devoted to metal ion/DOM complexation processes, this process has been ignored in the present work based on the following analysis:

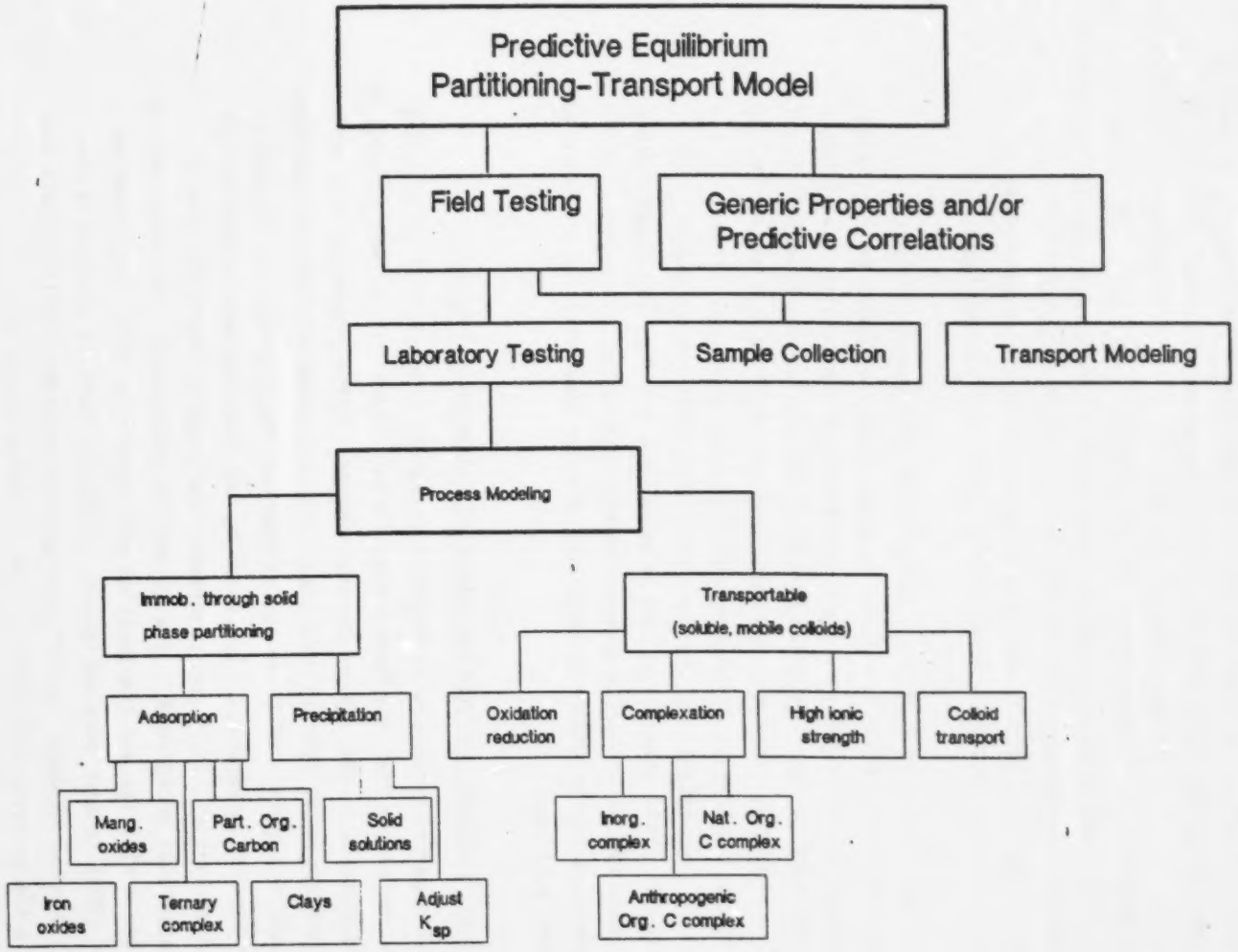

Figure 1. Schema for incorporating transport and geochemical process models into a prospective defensible regulatory tool.

Given:

- a generous groundwater organic carbon content can be estimated as 10 mg/L (25),
- a generous "complexation capacity" for a 10 mg/L fulvic acid solution can be estimated as 20 micromolar (estimated from 38),
- organic carbon is known to bind much more strongly to trivalent cations (e.g. Fe(III), Al(III) etc.) than to divalent of monovalent cations (2,5,8),
- a low amorphous-iron sandy aquifer material was characterized as possessing a porosity of 33% and an amorphous iron content of 0.077%.

Therefore:

- the quantity of amorphous iron exposed to 1 L of groundwater can be estimated by:
  total volume = 1 L/0.33 = 3 L
  solid volume = 3 - 1 = 2,000 cm^3
  solid mass = (2,000 cm^3)(2.5 g/cm^3) = 5,000 g
  (amorphous Fe mass = (5,000 g)(0.00077) = 3.85 g)
- the "molar" iron content available for complexation with DOM is therefore:

  [Fe] = 3.85/55.85 = 0.07 M
- the ratio of [Fe] to DOM complexation capacity (CC) is then:

  [Fe]/CC = 0.07/20E-6 = 3500.

This exercise suggests that, under equilibrium conditions in a low amorphous iron content aquifer material, iron (and other major ions commonly found in groundwater) may tend to out-compete potentially toxic transition metals for DOM complexation sites.

The high ionic strength term listed under the transportable category in figure 1 represents potential difficulties in estimating ionic activity coefficients at higher ionic strengths. The two activity coefficient algorithms in MINTEQA2 include the Davies extension (10) and the extended Debye-uckel expression with the (17) procedure for estimating neutral species activity coefficients (37). The Davies extension is believed to be adequate for ionic strengths less than 0.5 M; the extended Debye-Huckel procedure is presumably even more robust. Because most shallow groundwaters have ionic strengths in the range of 0.01 to 0.001 M, errors in activity coefficient correction estimates should be relatively minor or non-existent.

The possibility of insoluble contaminant migration via colloidal particle transport is a relatively recent concern in the scientific literature (7,9,15, 21,28). If colloidal particles are ubiquitous and if they bind significantly with contaminants, then this phenomenon must be accounted for in predictive transport and fate modeling efforts. Research on colloidal particles formation, aggregation and transport is the subject of extensive research by many investigators.

The last category in the transportable section of figure 1 includes the oxidation-reduction potential. Virtually all of the 14 potential inorganic contaminants of concern to the EPA Office of Solid Waste (Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn) can display partitioning behavior that is either directly or indirectly influenced by the redox status of the groundwater. The difficulties associated with obtaining experimental estimates of the thermodynamic Eh of low temperature groundwater systems is well known (23,24,31,40). In addition, low temperature systems may be inherently in disequilibrium (32). Given these difficulties, the present approach for accounting for Eh includes: (1) focusing both laboratory experimentation and modeling efforts on individual ionic species [i.e., As(III), As(V), Cr(VI), Se(IV), and Se(VI)], (2) statistically characterizing groundwater chemistry (i.e., use distributions including the absence or presence of sulfides), and (3) development of new analytical methodologies for measuring Eh and accounting for disequilibrium effects.

Physico-Chemical Processes Influencing Potential Contaminant Immobilization

The second major category in the base of the pyramid in figure 1 includes processes that may immobilize contaminants through solid phase partitioning. Unlike those processes that may render contaminants transportable, ignoring any of the processes that may immobilize contaminants is considered conservative from a regulatory standpoint. Specifically, scientific accuracy is desirable; however, errors in the process models must lie in a conservative direction as a matter of regulatory policy.

Of all the processes that may immobilize contaminants, those that lead to precipitation of highly crystalline pure mineral phases are the best understood and have received the most scientific scrutiny. Potential contaminant immobilization through amorphous phase or solid solution formation processes may be significant, however, these processes are insufficiently understood (or documented) to permit their current assessment on a routine basis. For example, preliminary work on the pH-dependent partitioning of Ba indicates that a solid solution component

may be necessary for interpreting laboratory data. In an analogous manner, as will be demonstrated in a later section of this paper, the pH-dependent behavior of Cd is best described by the formation of an amorphous $CdCO_3$ phase.

The second major immobilization process, adsorption, has received considerable attention in both "Multiphase" soils partitioning studies and pure phase laboratory studies. It is well known that pure amorphous and crystalline hydrous oxides of iron, manganese, silica, and aluminum--in addition to aluminosilicate and particulate organic carbon phases--can all exhibit differential, pH-dependent adsorption affinities for ionized inorganic contaminants. Difficulties in quantitatively modeling adsorption in a multiphase sediment can be grouped into at least two general areas. First, there exists an experimental inability, at present, to definitively discern those interfacial processes limiting contaminant solubilities. With present scientific knowledge, it is clear that the adsorptive process may serve either as an intermediate step in a precipitation process or as a solubility limiting process in itself. Mathematically, this experimental limitation translates into a conclusion given by Westall and Hohl (39). They suggested that, for a given set of experimental data, simple adsorption models can describe surface amphiprotic behavior with a facility equal to that of sophisticated techniques. Second, with the present implementation strategy, a multiphase sediment is viewed as a collection of independent phases. More recent work (18,19) suggests that metal adsorption in a multiphase system may or may not be additive (with respect to the sum of the individual contributors).

The selection of the MIT Diffuse Layer Adsorption Model (MIT DLM-(12)) for the present modeling effort was based on an attempt to address several limitations in addition to those given above. For example, an advantage with the MIT DLM is the built-in database of intrinsic adsorption constants. Figure 2 displays relationships observed in the literature (12,33,35) between the log metal ion first hydrolysis constant and the intrinsic adsorption constants required for a variety of models and pure phase surfaces. Two points can be discerned from figure 2. First, periodicity can be observed in the adsorption behavior of metals on hydrous oxide surfaces. This periodicity can be used both to identify anomalies in experimental data and to predict intrinsic adsorption constants when experimental data are unavailable. Second, given that these constants were obtained for a wide variety of surfaces and significantly different models, the slopes of these relationships are remarkably similar, which suggests that these models may be approaching a more fundamental thermodynamic understanding of interfacial processes.

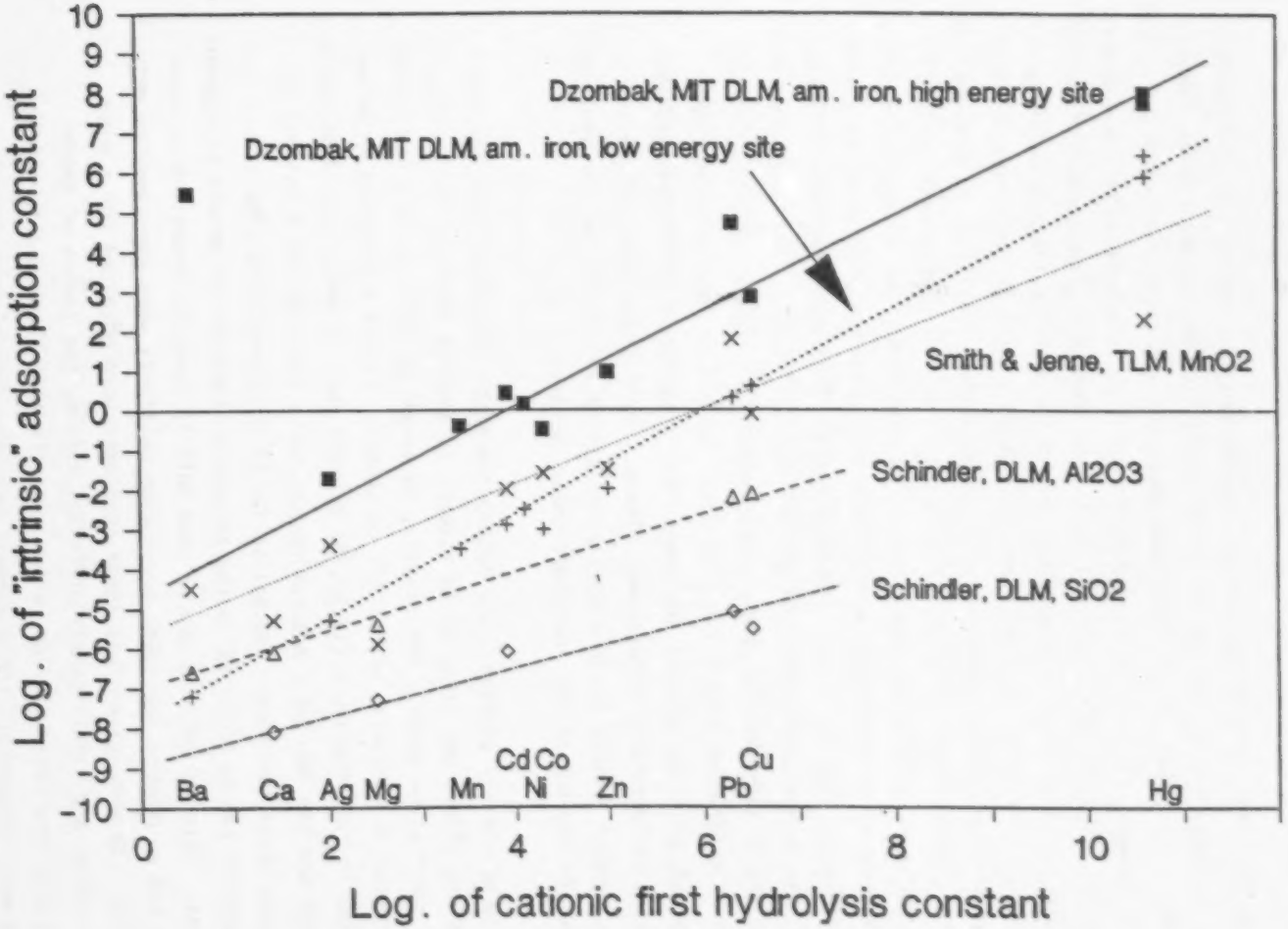

Figure 2. Relationships between metal ion first hydrolyses constants and intrinsic adorption constants for a variety of surfaces and three adsorption models.

All three models given in figure 2 describe "surface complexation" between metal ions and, for example, an adsorptively active iron oxide site (-FeOH) in terms of the following general relationship.

$$K_{ads,\ Me} = \frac{[=FeOM^{z-1}][H^+]EXP(-e\psi\ /kT)}{[=FeOH][M^{z+}]EXP(-ze\psi\ /kT)} \qquad (1)$$

Equation 1 is analogous to a solution complexation counterpart where a metal ion exchanges for a proton. The principal difference is that estimates of mobile ion concentrations (H^+ and M^{z+}) are modified by the Boltzmann expression [EXP(-zeψ /kT), where ψ = "interfacial electrostatic potential", Z = ion valence, e = electron charge, k = Boltzmann constant, T = absolute temperature]. The surface potential can seldom be determined experimentally without ambiguity. It is more commonly estimated using the Gouy-Chapman one-dimensional solution to the Poisson-Boltzmann charge/potential relationship in conjunction with zero (MIT DLM; simple DLM), one (4), or two (Triple Layer Model, 11) capacitative relationships.

From a preliminary sensitivity analysis, the electrostatic terms in equation 1 tend to have a second-order effect on the predictions of metals partitioning behavior (especially when compared to variations in groundwater pH). The surface potential term has been retained in our current effort for four reasons. First, surface potential terms are required in current Derjaguin-Landau-Verwey-Overbeek based models of colloidal particles stability. Second, electrostatic surface charge terms have been useful in describing perturbations in adsorbed state pH-sensitive organic compound degradation processes (16,29). Third, electrostatic terms may be important for describing metals partitioning behavior in very low ionic strength groundwater systems. Fourth, with the MIT DLM, there are no additional model input parameters needed with or without an electrostatic term.

Comparison of Experimental Data With Model Predictions

The data presented in figures 3 and 4 summarize the results obtained in a recent study on saturated zone aquifer materials (26). From a preliminary study to examine the pH-dependent partitioning behavior of cationic inorganic contaminants on

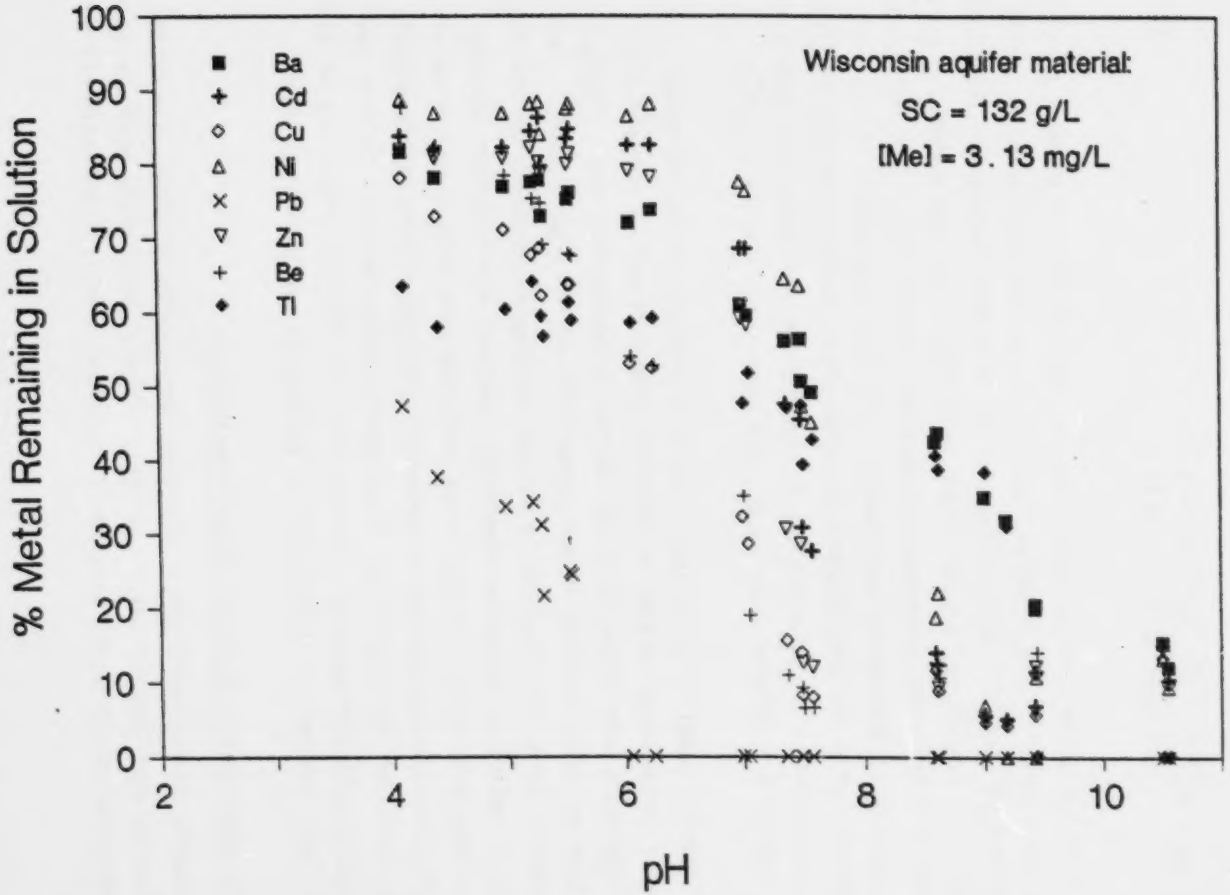

Figure 3. Experimetal pH-dependent partitioning data for Ba, Be, Cd, Cu, Ni, Pb, Tl, and Zn with the high sand content Wisconsin aquifer material.

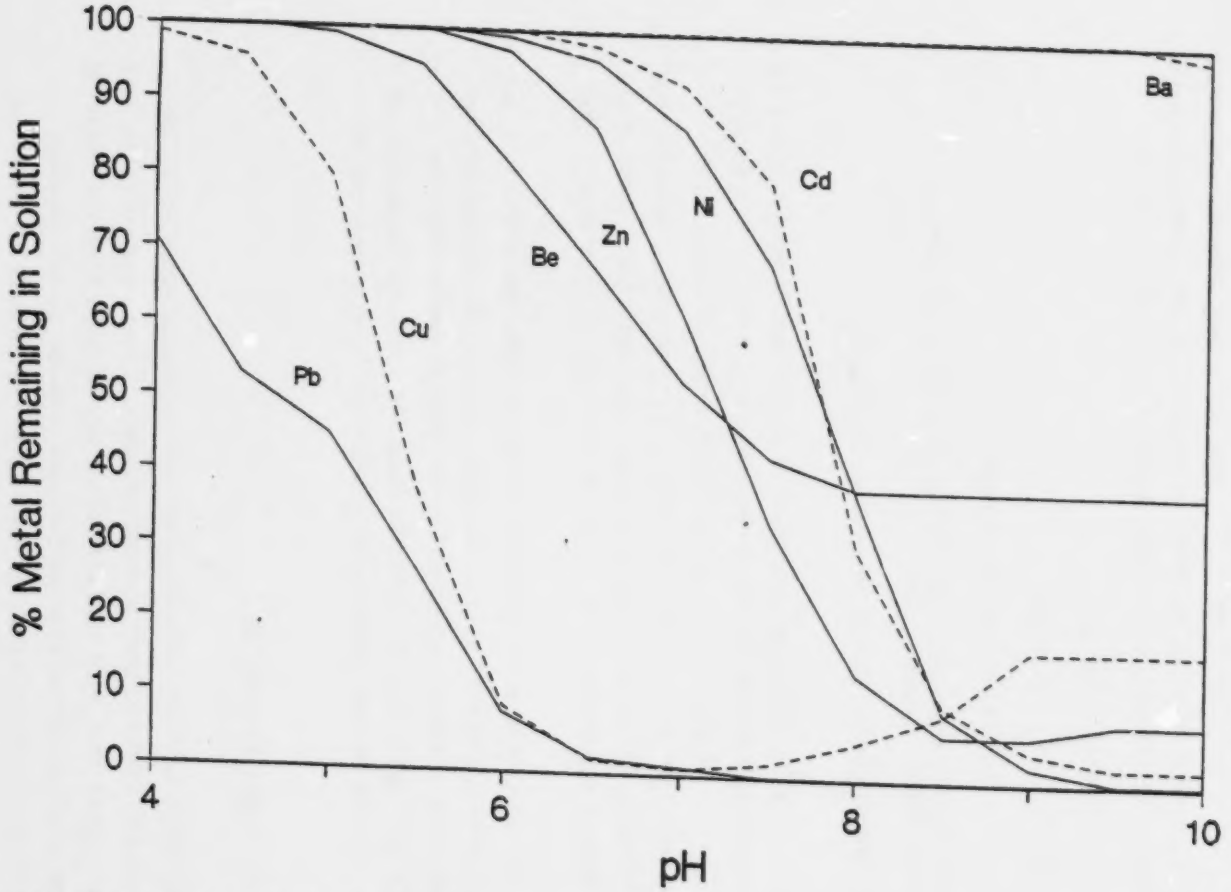

Figure 4. MINTEQA2 simulations of the data depicted in figure 3. Partitioning mechanisms include adsorption with aquifer material amorphous iron and precipitation of insoluble hydroxides, sulfates, and carbonates.

aquifer materials, it was observed that the Wisconsin material--a high sand content (99.3%), low cation exchange capacity (7.1 cmol/kg), and low amorphous iron content (0.077%) sediment--had the least affinity for eight cationic contaminants (Ba^{2+}, Be^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Tl^{+}, and Zn^{2+}) over the pH range from 4 to 9. Subsequently, a more detailed sequence of 48-hour, batch, adsorption experiments was conducted with the following experimental procedures/conditions:

Solids Concentration = 132 g/L

Initial $[Me^{z+}]$ = 3.13 mg/L

T = 25 degrees Centigrade

Analysis by Inductively Coupled Plasma Atomic Emission Spectrometry (with Myers-Tracy Signal Compensation)

Separation by centrifugation for 46 minutes at 10,000 RCF.

Of the trace metals, only Ba and Zn were present at sufficient concentrations in the sediment to require adjustment for subsequent modeling efforts. In general, limiting equilibration to 48 hours was considered conservative because both adsorptive and precipitative mechanisms will lead to further loss of metals from solution with an increase in sediment exposure time. For additional details concerning the experimental procedures, the reader is referred to Loux et al. (26).

Figure 3 displays the pH-sensitive partitioning behavior observed with all eight cations on the Wisconsin aquifer material. As observed with all of the aquifer materials, Pb tends to be removed from solution far more strongly than any of the other elements. Ba and especially Tl tended to show the least pH dependence of all of the metals. In the mid-pH region, a general affinity sequence can be represented by:

Pb > Cu, Be > Zn > Cd > Tl > Ni, Ba

A comparison of the above affinity sequence with the sequences observed in the literature (12,13,14,30) leads to several observations. First, the relative positions of Pb and Cu suggest that hydrous oxide sites may be significantly removing these elements from solution rather than particulate organic carbon (hydrous oxides display affinity sequences ordinally related to the respective metal ion log first hydrolysis constants) (figure 2); organic carbon displays sequences more related to the (20) sequence (i.e., Cu is bound more strongly than Pb--1,27,36). Second, the position of Cd in the sequence suggests greater removal from solution

than would be expected by an adsorptive process on a hydrous oxide surface. Third, the relative position of Tl in the affinity sequence is strongly pH-dependent since Tl is strongly removed from solution at low pH conditions and weakly removed from solution at high pH values (relative to the other elements).

Figure 4 displays the results from MINTEQA2 simulations of the data given in figure 3. These simulations were performed including both adsorptive processes on the amorphous iron oxide (MIT Diffuse Layer Model; 12) and pure phase precipitation of $CdCO_{3,am}$, $BaSO_{4,am}$, $Pb(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$, and $Zn(OH)_2$. Figure 5 compares the experimental data (figure 3) with model predictions (figure 4) for Pb, Zn, Ni, Cd, and Cu. Those data points in figure 5 below the "zero" line represent conservative estimates (i.e., model-predicted soluble metal concentrations exceed experimental values).

From figures 3, 4, and 5, the behavior of Pb, Zn, and Ni was mainly conservative and best described by adsorptive phenomena. According to the model, at low pH conditions, adsorption was the only process limiting the mobility of these elements. The behavior of Cd, also mainly conservative was best described using a solubility constant for amorphous octavite ($CdCO_3$).

The behavior of Cu was not well described by the model; Cu may have formed soluble complexes with dissolved organic matter (not implemented in the model). From figure 5, the model predictions for Cu are not conservative.

The behavior of Ba was poorly described by both adsorption and solubility constraints from either amorphous or cystaliine barite. The solubility of Ba may be limited by a solid solution with calcite (a process not presently in the model).

The model simulations for Be were performed by: (1) ignoring an amorphous $Be(OH)_2$ phase (model simulations were not conservative), (2) ignoring aqueous phase hydroxy complexes (with the available complexation constants, the model simulations led to virtually zero removal from solution in the pH range of 4 to 9), and (3) including adsorptive phenomena where intrinsic adsorption constants were obtained using linear free energy relationships (12) with the log first hydrolysis constant (34). The adsorption envelope given for Be in figure 4 is promising although additional work is required.

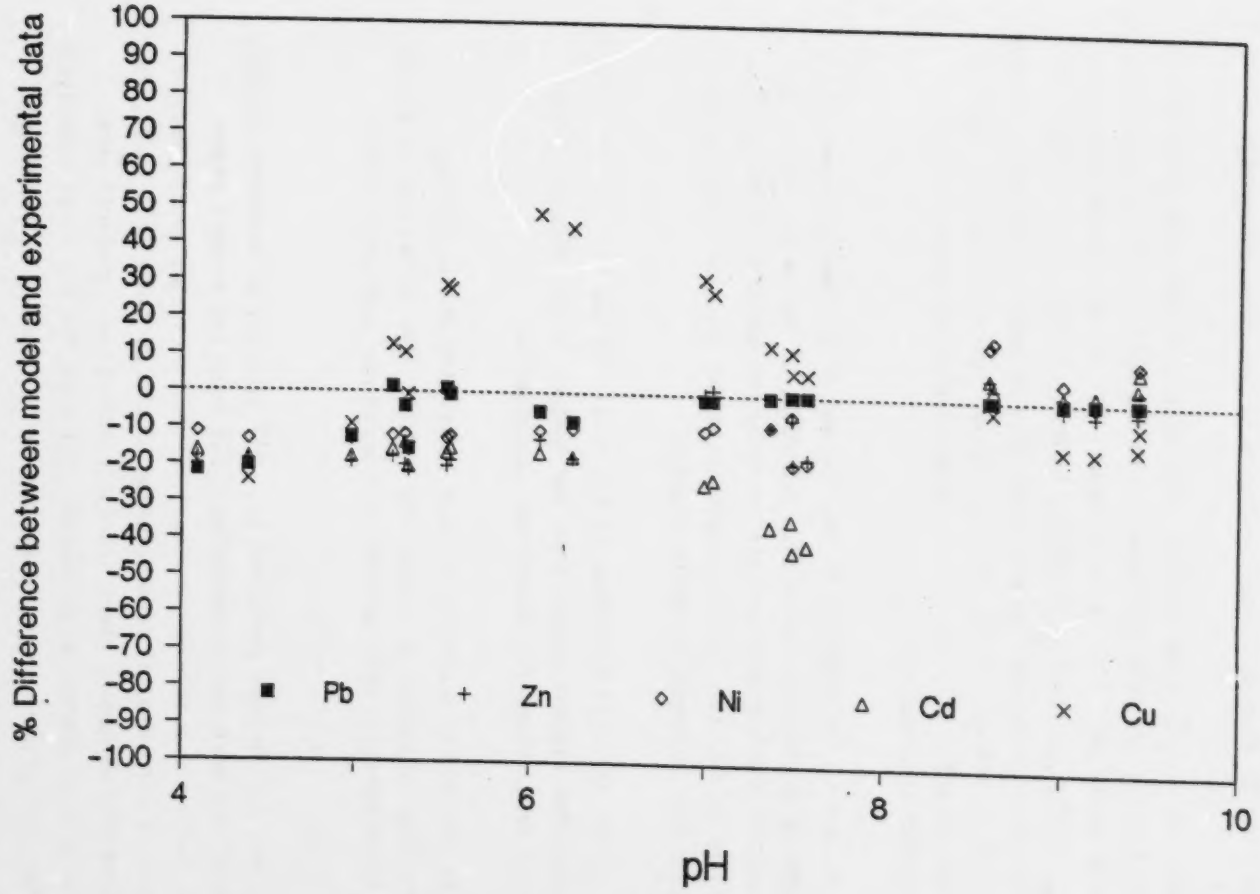

Figure 5. Comparison of experimental and modeled data as a function of pH for Pb, Zn, Ni, Cu, and Cd. Data points below the "zero" line represent conservative estimates; proximity to the "zero" line represents scientific accuracy.

Thalium the last element in figure 3, was not modeled and exhibited significant removal even at low pH conditions. At least two possible explanations can be given to describe the behavior of this element: (1) co-precipitation with Pb, and (2) adsorption on manganese oxides (14) with subsequent oxidation to insoluble $Tl(OH)_3$. Neither set of reactions are presently in MINTEQA2.

Several trends were observed in the comparison of experimental and modeled data. First, the pH-dependent partitioning behavior of three of the four elements expected to bind most strongly with amorphous iron were indeed best described by adsorption processes on aquifer amorphous iron (Cu being the one exception). Second, model predictions for solute metal concentrations at low pH conditions tended to be consistently conservative; one or more additional adsorptive phases will probably be required before the accuracy of model predictions is increased. Third, those elements not expected to adsorb strongly on amorphous iron oxide (Ba and Tl) display solubility limitations not presently addressed by the model.

CONCLUSIONS

Geochemical equilibrium models can be effectively used in risk assessments concerning potential groundwater migration of inorganic contaminants. The process of validating these models for regulatory purposes, however, will require a quantitative statistical overlay that will examine each process (and each ionizable species) on the degree of confidence in the ability to describe these processes. Validation in a regulatory sense differs from that associated with a scientific perspective in two fundamental ways. First, in those processes where uncertainty is significant, errors must be biased toward the conservative direction (i.e., protective of the environment). Second, depending on the statistical uncertainty, the final model will lie somewhere on a continuum between purely conservative assumptions and striving for absolute scientific accuracy.

The application of the principles of geochemical equilibrium theory to describe the partitioning behavior of inorganic ionizable contaminants will require a diverse collection of individual processes derived from a large collection of subdisciplines. Pure phase precipitation, solid solution precipitation, oxidation-reduction, complexation, and adsorption processes will all be involved in an operational model. With the present implementation strategy, however, time dependency (or kinetic) limitations to the common assumption of equilibrium must be addressed by judiciously either ignoring selected thermodynamic constants or adjusting the constants to describe phases characterized as being hydrous or amorphous.

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